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Solubilization of TCNQ by Anionic Surfactants

Shinya Muto, Yoshiaki Aono,* and Kenjiro Meguro
Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

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In a previous paper,[1] we reported on the remarkable coloration due to a charge transfer interaction between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and cationic surfactants when the former was solubilized into the latter. A similar phenomenon has been reported by Deguchi *et al.*[2] for the interaction between TCNQ and nonionic surfactants.

The present paper deals with the determination of the cmc of anionic surfactants by measuring the change in shape of the absorption spectrum of TCNQ due to its solubilization.

Experimental

Lithium dodecyl sulfate (LiDS), sodium dodecyl sulfate (SDS), potassium dodecyl sulfate (KDS) and triethanol ammonium dodecyl sulfate (TDS) were used as anionic surfactants. They were synthesized by the same method as described previously.[1] All products were extracted for about 200 hr with petroleum ether and recrystallized five times from water–isopropyl alcohol mixtures. No minima were observed in the diagram of surface tension against the concentration of anionic surfactants. 7,7,8,8-tetracyanoquinodimethane (TCNQ) was synthesized by the usual method[1] and recrystallized five times from acetonitrile. Sodium chloride of extra pure grade was subjected to ignition.

Water was purified by percolation of tap water through an ion-exchanger, followed by distillation from alkaline potassium permanganate in a pyrex still. The specific conductance of water was $(1\sim1.9)\times10^{-6}$ ohm^{-1} cm^{-1} at 25 °C.

Solubilization measurement: the procedure was essentially the same as that described previously.[1] TCNQ (3 mg) was added to anionic surfactant solutions (15 ml) in L-type tubes and shaken for about three days (72 hr) in a water thermostat at 40 ± 0.1 °C. After shaking, excess TCNQ was filtered off through glass filters. The absorption spectra of the samples were measured in 10 mm cells with a spectrophotometer (Hitachi EPS-3T) at 40 ± 0.1 °C. The measurement was carried out on the same day as filtration, usually within 3 hr of filtration because of slow fading of color of the TCNQ-surfactant micelle complex solution.

Surface tension: measured with a Wilhelmy-type surface tensiometer (Shimazu ST-1) at 40 ± 0.1 °C, the value obtained with 10 min of dipping being defined as surface tension.

Conductance: specific conductance was measured with a conductometer (Toa Electronics Model CM-1DS) and conductivity cell (Toa Electronics Type CG-201PL) at 40 ± 0.1 °C.

Results and Discussion

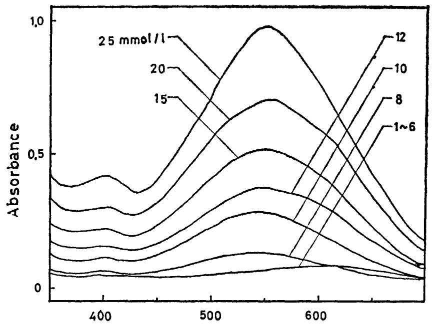

Fig. 1. Absorption spectra of TCNQ solubilized in SDS solutions. Figures show concentration of SDS solutions.

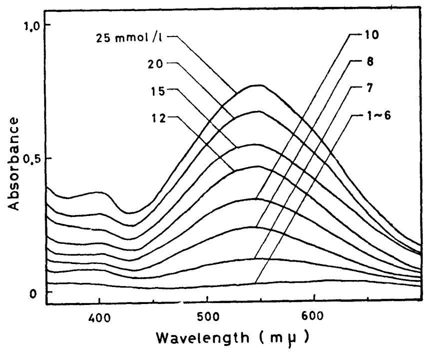

Fig. 2. Absorption spectra of TCNQ solubilized in TDS solutions. Figures show concentration of TDS solutions.

Remarkable coloration took place when TCNQ was solubilized in anionic surfactant solutions above cmc. The coloration was observed one day after the start of shaking in a thermostat at 40 ± 0.1 °C. It increased gradually and reached equilibrium after about 72 hr. At equilibrium the color of TCNQ solubilized in LiDS, SDS, KDS, and TDS solutions was blue-purple, being almost the same for them all when observed with the naked eye. The absorption spectra of TCNQ solubilized in SDS and TDS solutions are shown in Figs. 1 and 2, respectively. Almost the same absorption spectra were observed for the other two surfactants. TCNQ in the solubilized state has absorption maxima

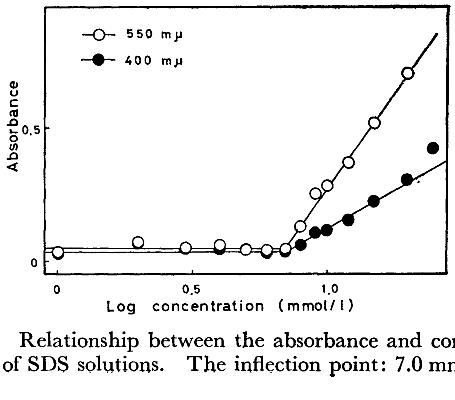

Fig. 3. Relationship between the absorbance and concentration of SDS solutions. The inflection point: 7.0 mmol/l

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* Present address, Dic-Hercules Chemicals Inc., Dic Building, No. 3, Tori, 3-chome, Nihonbashi, Chuo-ku, Tokyo.

[1] S. Muto, K. Deguchi, Y. Shimazaki, Y. Aono, and K. Meguro, This Bulletin, **44**, 1087 (1971).

[2] K. Deguchi and K. Meguro, *J. Coll. Interface Sci.*, **38**, 596 (1972).

Table 1. Critical micelle concentration of anionic surfactants by electroconductance, surface tension and solubilization of TCNQ at 40 °C

Surfactant	Electro-conductance (mmol/l)	Surface tension (mmol/l)	Solubilization of TCNQ (mmol/l)
LiDS	8.4	7.0	7.6
SDS	8.1	6.8	7.0
KDS	7.4	6.6	5.8
TDS	6.2	5.5	6.0
Salt solution of SDS (concentration of NaCl)			
10 mmol/l	5.5	4.4	4.6
20 mmol/l	3.6	3.0	3.3

at 400 and 550 mμ above cmc but below, no remarkable absorption was observed except for some slight absorption bands at 400 and 620 mμ. Their intensities were very weak and broad. The intensities of the bands at 400 and 550 mμ increased rapidly above cmc with concentration of the surfactant.

Figure 3 shows the plot of the optical density at 400 and 550 mμ against the logarithm of surfactant concentration, in which the inflection point coincides with the cmc value. The cmc values of anionic surfactants obtained by this method are summarized in Table 1. They agree with those obtained by surface tension and electroconductance methods.

The effect of addition of sodium chloride on the spectrum of TCNQ solubilized into aqueous solution of SDS is shown in Fig. 4. The shape of the absorption spectrum is almost the same as that shown in Fig. 1. However, it was found that the addition of salt increased the intensity of the band of solubilized TCNQ and decreased the cmc of SDS. The cmc values measured in the presence of salt are given in Table 1. Increase in the intensity of the band of solubilized TCNQ by addition of salt is of particular interest (Fig. 4).

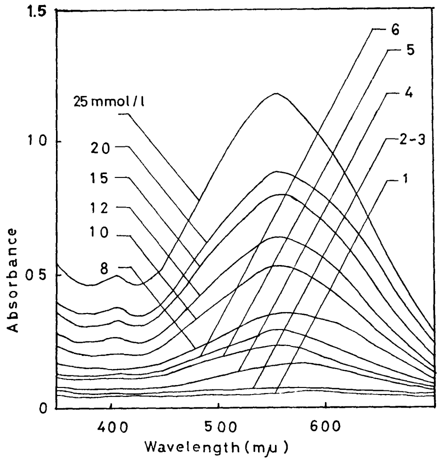

Fig. 4. The effect of addition of sodium chloride on the absorbance of spectrum of TCNQ solubilized into aqueous solution of SDS. Concentration of sodium chloride: 20 mmol/l. Figures show concentration of SDS solutions.